ELECTRONIC STRUCTURE OF ULTRANANOCRYSTALLINE DIAMOND GRAIN BOUNDARIES

Basic Energy Sciences

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ANL-MSD

Motivation

- **Goal:** to gain an understanding of properties of ultrananocrystalline diamond (UNCD) and influence of impurities using electronic structure methods.

Problems:

Where are nitrogen impurities located in UNCD?

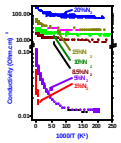
What is the effect of nitrogen on electronic properties?

What is the effect of hydrogen on UNCD properties?

Background

Structure of UNCD

- Electron diffraction and UVRaman spectroscopy show that the UNCD films are phase-pure diamond.
- TEM shows microstructure consisting of crystallites with an average size of 3-10 nm separated by narrow grain boundaries.
- Up to 10% of carbon atoms are located in the grain boundaries. Grain boundaries play a crucial role in determining the properties.



Impurities

- Nitrogen is introduced during the film growth to modify properties. Nitrogen strongly increases conductivity of UNCD.

Density-Functional Based Tight-Binding Method

- Kohn-Sham orbitals are expressed in terms of explicit minimal sp basis set of atom-centered valence electron orbitals.
- Two center approximation (three-center and crystal-field integrals to the matrix elements are neglected).
- The generaleigenvalue problem for many-atom configuration is solved to determine the one-electron energies.
- Interatomic forces for molecular dynamics are calculated from analytical gradients of the total energy.
- The total energy is a sum over a "band structure energy" and a short-range repulsive pair-potential, E_{rep}, fitted to self-consistent field calculations.
- The self-consistent charge scheme is based on the second order term in an expansion of energy over electron density fluctuations. This energy term is expressed through Mulliken charges and calculated self-consistently at each simulation step.

M.Elstner, D.Porezag, G.Jungnickel, J. Elsner, M.Haugk, Th.Frauenheim, S. Suhai, G. Seifert, Phys. Rev. B, **58**, 7260,1998

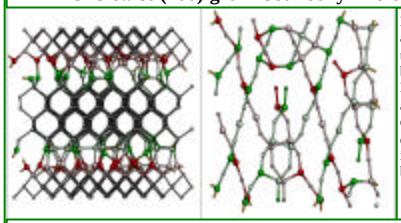
MD simulation of twist grain boundaries

- (100) represents a general diamond surface, it has two broken bonds per atom as any other surface except (111) and (110).
- Twist (100) grain boundaries represent general high-energy high-angle grain boundaries.
- Three twist (100) grain boundaries: Σ5, Σ13 and Σ29 were studied.

Simulation details

- Each periodic cell has two grain boundaries and total of 16 layers (208 atoms for Σ13, 320 for Σ5 and 464 for Σ29).
- Simulated annealing started at elevated temperature (1500K and 5000K) that was gradually lowered.
- The final structure was optimized by a conjugate gradient method.

Σ29 twist (100) grain boundary in diamond



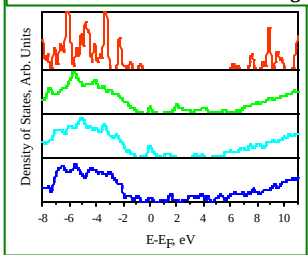
Large red (green) atoms are in the upper (lower) grain boundary plane. Bright (pale) atoms are three-(four-) coordinated. Smaller colored spheres are in second grain boundary plane.

DFTB results on structure of twist grain boundaries.

GB	α, deg.	ΔV,%	ΔE, eV	sp^3,%	sp^2,%	sp^{2+x},%
Σ5(2□ 2)	53.1	14	1.55	54	11	35
Σ13	67.4	14	1.57	54	23	23
Σ29	43.6	10	1.54	45	28	28

- About 45% of all atoms in the grain boundaries are three-coordinated.
- Disorder is confined to two interface planes.

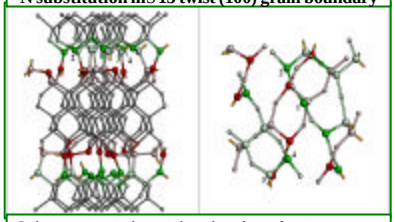
Electronic structure of grain boundaries



- Plots are normalized by the number of atoms.
- Peaks in the grain boundary plots are broader due to disorder.
- Features in the bandgap are due to double and dangling bonds and distortion.
- All three GB plots have similar features.

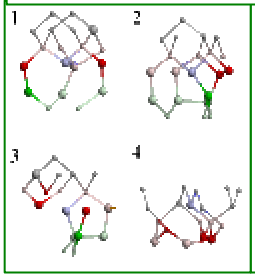
- Electronic levels in the diamond bandgap are localized on the grain boundary atoms.
- All three high-energy grain boundaries have similar geometry and electronic spectra.
- Σ13 (100) grain boundary can be used as a model for a general high-energy high-angle grain boundary.

N substitution in Σ13 twist (100) grain boundary



Carbon positions in the grain boundary chosen for nitrogen substitution are numbered 1, 2, 3 and 4.

Final configurations of N atom in the grain boundary



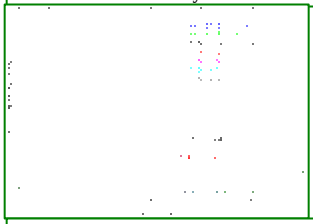
Four typical substituional sites were chosen. Final positions are on the left.

site	initial	final	E, eV
1	sp^{2+x}	sp^{2+x}	-0.6
2	sp^2	sp^2	0.7
3	sp^3, GB	sp^1	1.7
4	sp^3, 2nd layer	sp^{2+x}	2.6
bulk	sp^3	sp^{2+x}	4.9

Nitrogen moves to three-coordinated position.

Substitutional energy of N in the GB is much lower than in the bulk.

Total and Local Density of States for Σ13 Grain Boundary with N

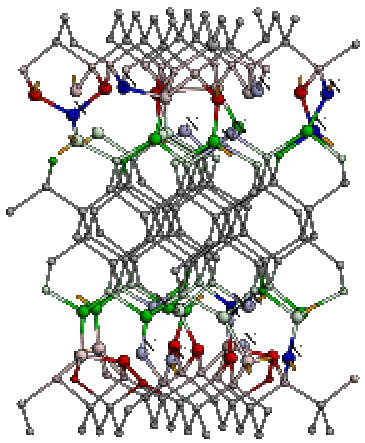


- Empty N states are marked with (*).
- Peaks in the band gap of diamond arise from the grain boundary atoms.
- Nitrogen contributes to the states in the gap.

No shallow nitrogen donor for conduction band

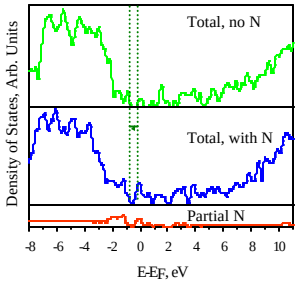
Nitrogen can increase conductivity related to carbon π^*-states

Σ13 grain boundary with higher N content



- Assuming that all nitrogen is in the GBs, 3% of N in the film gives 30% N in the grain boundaries.
- Nitrogen atoms do not cluster but rather avoid each other.

Electronic structure changes at high nitrogen content

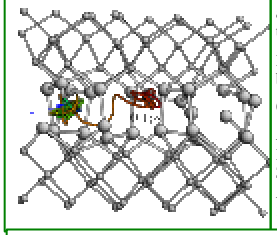


A shift of occupied states relative to the Fermi level is schematically shown with an arrow.

Upward Fermi level shift of about 0.4 eV.

This shift can increase conductivity related to carbon π^*-states.

Hydrogen Addition to Σ13 twist (100) grain boundary



MD path of H atom during initial annealing. The color changes from red to blue as time progresses.

Hydrogen atoms diffuse in grain boundary at 1200K and up.

Optimised geometry:

Average Binding Energy of Hydrogen:
3.5 eV
Average C-H Bondlength:
1.1Å

Hydrogen addition increases carbon coordination and decreases density of states in diamond band gap.

Conclusions

- Twist grain boundaries in diamond result in 40%-50% of three-coordinated atoms in the interface.
- Nitrogen is much easier to incorporate into the grain boundary than into the bulk diamond.
- Nitrogen atoms are responsible for Fermi level shift of about 0.4 eV. This can increase conductivity.
- Hydrogen saturates dangling bonds and does not improve electrical properties of UNCD.

Future work

- Electronic transport modeling of UNCD with nitrogen will help to understand dependence of conductivity on nitrogen concentration.
- Tight-binding modeling of interactions between different impurities will help to identify possible formation of complexes, e.g. nitrogen-hydrogen defects.
- Other elements that could modify properties of UNCD will be studied, e.g. B, S and P.
- These studies will be used to guide experimental developments of UNCD films.

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